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Doped $GdCl_3$ high resolution thermometers for use near to the lambda point

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The paramagnetic salt $GdCl_3$ was doped with the diamagnetic La^{3+} ion, depressing its Curie temperature (T_c) from 2.2 K to 2.185 K. A paramagnetic salt thermometer was constructed using this salt and measurements were made of its sensitivity, noise, and drift.

Gadolinium chloride Lanthanum chloride

1 INTRODUCTION

The superfluid transition of liquid ^{4}He provides an excellent testing ground for renormalisation group theory predictions in non-equilibrium phase transitions [1]. In order for these predictions to be tested, very precise measurements are required close to the transition. This demands a high degree of both temperature control and precision. The high-resolution thermometer (HRT) used in such experiments consists of a paramagnetic salt pill tightly coupled to a superconducting pick-up coil. A superconducting flux tube, surrounding the HRT, is used to trap a very stable DC field (~10 mT). The salt is thermally coupled to the helium sample through a grid of high purity (99.999%) copper heat fins. The pick-up coil is connected to a SQUID, which measures changes in the magnetisation of the salt as a function of temperature.

Ideally, these thermometers should be operated with the salt pill in the paramagnetic phase and close to T_c where its magnetisation is highly temperature dependent. In the ferromagnetic phase, discontinuous changes in the flux density - the Barkhausen effect [2] - can appear as a significant noise contribution in the thermometer measurements. Most HRTs [3] use salt pills made of crystalline copper ammonium bromide [$Cu(NH_4)_2Br_4 \cdot 2H_2O$] (CAB) which has a T_c of approximately 1.8 K. Recent designs use $GdCl_3$, which is chemically less reactive than CAB and can be grown directly onto the copper fins. In addition, $GdCl_3$ has a T_c of 2.2 K and is five times as sensitive as CAB at the superfluid transition temperature, T_λ (2.1768 K under saturated vapour pressure).

Despite these favourable properties, T_c for $GdCl_3$ lies just above T_λ, causing the salt to operate in the ferromagnetic phase. In an attempt to overcome this problem, we doped $GdCl_3$ with La^{3+}, a non-magnetic ion, in order to depress its Curie temperature. $GdCl_3$ and $LaCl_3$ are isomorphous salts. In a solid solution, the diamagnetic La^{+3} ions substitute for the paramagnetic Gd^{+3} ions to form crystals in which the ions of both salts are present [4]. For a non-magnetic ion such as La^{3+}, the depression in T_c is expected to be approximately linear with doping concentration [5].

2 EXPERIMENT

2.1 Sensitivity measurement

We added 94.5 g of $GdCl_3 \cdot 6H_2O$ to 2.7 g of $LaCl_3$ to produce 63.74 g of $Gd_{0.9585}La_{0.0415}Cl_3$. The hydrated $GdCl_3$ was first dehydrated, using a reflux condensing technique, with thionyl chloride [6]. The $GdCl_3$ was then mixed with the $LaCl_3$ in a dry nitrogen atmosphere, and heated until the sample melted. The molten salt was poured into a BeCu capsule, flowing in-between the enclosed copper heat fins, and left to solidify. The assembly was sanded to remove excess salt and sealed, using a BeCu cap and cadmium solder. BeCu was chosen in order to reduce background noise caused by current fluctuations in the capsule wall, while maximising thermal conduction to the salt pill. A superconducting pick-up coil fit tightly around the capsule. Its dimensions were optimised to match the input impedance of the SQUID and to cover the salt adequately, ensuring maximum energy transfer. A thin Niobium capillary shielded the twisted pair leads of the pick-up coil. The capsule was soldered to an OFHC (oxygen free high conductivity) copper rod that was in thermal contact with a helium reservoir (Fig. 1). A number of HRTs were constructed, three of which where mounted in thermal contact with the helium.

The helium reservoir was separated from a surrounding liquid helium bath by a three-stage thermal isolation system, located inside a vacuum can. The first two stages were controlled to within 10 μK using calibrated germanium resistance thermometers (GRT). The third, and innermost, isolation stage formed a shield completely surrounding the reservoir and the HRTs. Its temperature was regulated to within 0.1 μK by a servo system using a fourth HRT, made with a salt pill of pure $GdCl_3$.

Sensitivity versus temperature measurements were made for both the pure and doped $GdCl_3$ HRTs by slowly cooling the helium sample and recording the output of the HRTs and the GRTs simultaneously. The sensitivity of each thermometer is plotted versus temperature in Fig. 2. The sensitivity is defined as the change in the number of magnetic flux quanta, Φ_0, recorded by the SQUID magnetometer over a given change in temperature, as measured by the corresponding GRT.

The pure $GdCl_3$ HRT had a maximum sensitivity of 28.9 $\Phi_0/\mu K$ at 2.200 K, while the doped HRT had a maximum sensitivity of 23.6 $\Phi_0/\mu K$ at 2.185 K. This clearly demonstrates that the Curie temperature had been depressed. However, the depression in T_c by 0.7% was smaller than expected for a 4% La concentration [5], and the lower T_c is still above the temperature range for our experiments conducted very near to T_λ. This is thought to be due to inhomogeneous doping of the $GdCl_3$ salt, due to clustering of the $LaCl_3$ while the salt solidified. $LaCl_3$ has a melting temperature of 860°C compared to 609°C for $GdCl_3$ [7]. The reduction in sensitivity, by 18%, is thought to be due to the anisotropic susceptibility of $GdCl_3$ [8].

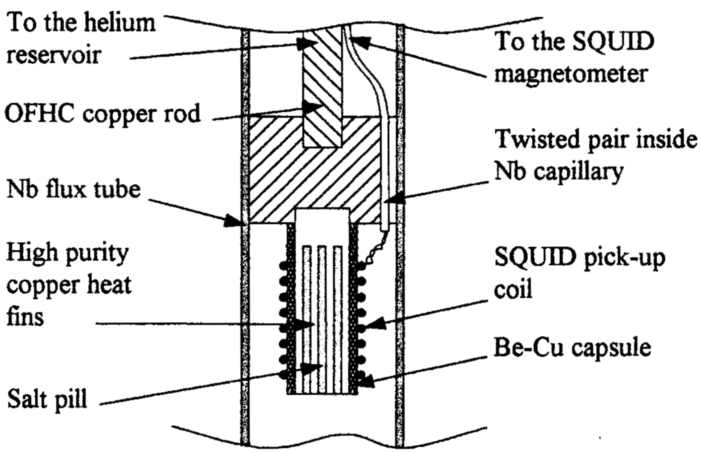

Figure 1

Schematic of the HRT

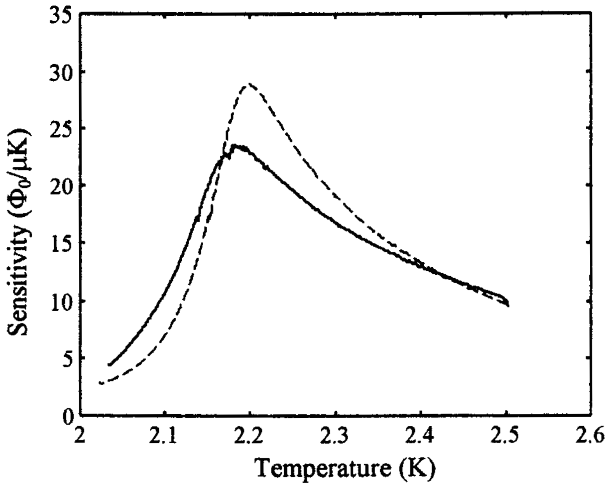

Figure 2

Sensitivity versus temperature data for $GdCl_3$ (dashed line) and La doped $GdCl_3$ (solid line) HRTs.

2.2 Noise measurement

To measure the thermal noise density, the isolation system was adjusted such that the cooling rate was less than 0.01 nK/s. Measurements were taken 5 mK below T_λ. The output of the HRT was filtered at 10Hz, connected to a spectrum analyser and the power spectral density (PSD) determined. (Fig. 3)

In a thermometer, one source of fluctuation noise is temperature variation due to energy fluctuations through the thermal link to the reservoir. If all other sources of noise are negligible, this temperature noise defines a thermodynamic limit. The Fluctuation-dissipation theorem (FDT) predicts a specific relation for this thermal noise density [9,10]:

$$\left(T^2\right)_{f+} = 4\tau k T^2 / C\left(1 + 4\pi^2\tau^2 f^2\right) \tag{1}$$

where $\left(T^2\right)_{f+}$ is the temperature noise density defined for positive frequencies. Here τ and C represent the thermal relaxation time and heat capacity, respectively, of the salt pill. They are related by $\tau = RC$, where R is the thermal impedance between the salt pill and the helium sample. As can be seen, in the low frequency limit, Eq. (1) reduces to $\sqrt{4Rk_BT^2}$. Therefore R is the only relevant parameter that can be adjusted in order to reduce noise originating from thermal fluctuations [11].

Agreement with the FDT can be sought by fitting Eq. (1) to the noise spectrum. This requires knowing the value of τ and C for the salt pill. The heat capacity was measured directly by a heat pulse technique, with the helium reservoir empty. After taking into account the additional heat capacity of the copper reservoir, each salt pill was determined to have $C = 82 \pm 2$ mJ/K. This agreed with an estimate of C calculated using the volume of the salt (0.24 cm^3), the density of $GdCl_3$ (4.52 g/cm^3) [7], and the zero field heat capacity data of Hovi *et al* [12]. Attempts were made to determine τ by applying heat to the helium reservoir when full. Unfortunately, the heaters used had response times greater than 1s and the salt pill relaxation time had to be determined from the fit to the noise spectrum.

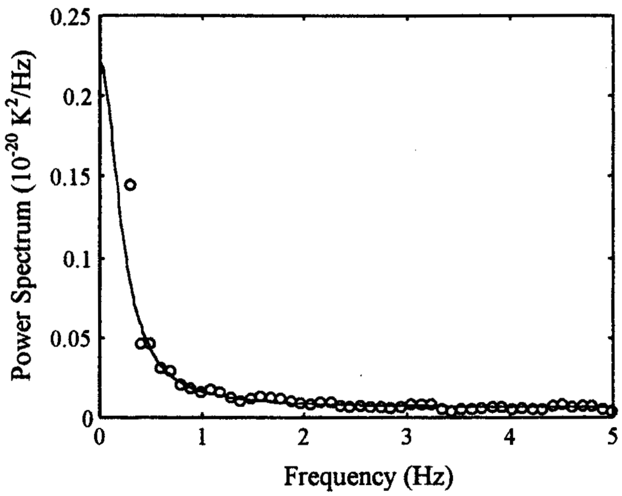

Figure 3

Noise spectrum for the La doped $GdCl_3$ HRT (circles). FDT fit (solid line)

The fit to the noise spectrum, shown in Fig. 3, yields $\tau = 0.7 \pm 0.1$ s. This gives an estimate for the thermal impedance of $R = 8.5 \pm 1.5$ K/W. At low frequencies, the noise density is 5×10^{-11} K/$\sqrt{\text{Hz}}$, which agrees with the noise measurement [11] of HRTs constructed with salt pills of pure $GdCl_3$. The PSD was found to contain a small but observable background noise, due to Johnson current noise in the capsule assembly. This was confirmed from measurements of a 'dummy' capsule, where the salt pill was absent. By disassembling the capsule and taking noise measurements of each component, it was shown that most of the current noise originated from the copper heat fins, and not from the BeCu capsule or the copper thermal link. This background noise had a magnitude of 1.8×10^{-4} $\Phi_0/\sqrt{Hz}$.

2.3 Drift measurement

All HRTs exhibit small drift rates that must be taken into account when making precise measurements over long periods. The origin of drift is not known but is thought to be due either to flux creep in the Niobium flux tube, or thermal relaxation of the salt pill that causes changes in its magnetisation. It has been observed [13] that, following the initial cool down of the salt pill, the drift rate decays to a constant value over a period of several days. Even small temperature changes 're-energise' the drift, which then decays with a faster time constant back to a steady value.

The drift rate was determined from measurements of the lambda point, taken over several hours, by slowly heating and then cooling through the superfluid transition. The lambda point was then used as an absolute temperature marker, to which any relative drift in the HRT flux output could be resolved. We measured the drift rates of the doped HRTs several times, during a six-month run. They had approximately constant drift rates of 1×10^{-12} K/s, in a direction such that the lambda point appeared to drift upwards in temperature. Since all the HRTs drifted in the same direction, we also have to consider the possibility that the lambda point itself was drifting, due to a small reservoir leak. The reservoir was filled at constant volume and sealed with a mechanical valve. This implies that our drift rate is an upper limit and may be smaller than measured. For comparison, the drift rates of pure $GdCl_3$ and CAB HRTs are $\leq 1\times10^{-12}$ K/s and $\leq 1\times10^{-13}$ K/s respectively [13].

3 CONCLUSION

By doping the paramagnetic salt $GdCl_3$ with a 4% Lanthanum concentration, we have depressed its Curie temperature by 0.7%. With improved doping homogeneity, it is proposed that this displacement could be finely tuned as a function of the amount of Lanthanum added to the salt. The low frequency noise levels and drift rates are equivalent to those of HRTs made with salt pills of pure $GdCl_3$. The noise spectrum is found to be in very good agreement with the predictions of the fluctuation-dissipation theorem, indicating that we have reached the thermodynamic noise limit. Further improvements in noise levels may be achieved by both carefully re-designing the HRT to reduce the current noise and reducing the thermal impedance between the salt pill and the helium sample.

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